

## 4.7 Waste Solvent Reclamation

### 4.7.1 Process Description<sup>1-4</sup>

Waste solvents are organic dissolving agents that are contaminated with suspended and dissolved solids, organics, water, other solvents, and/or any substance not added to the solvent during its manufacture. Reclamation is the process of restoring a waste solvent to a condition that permits its reuse, either for its original purpose or for other industrial needs. All waste solvent is not reclaimed, because the cost of reclamation may exceed the value of the recovered solvent.

Industries that produce waste solvents include solvent refining, polymerization processes, vegetable oil extraction, metallurgical operations, pharmaceutical manufacture, surface coating, and cleaning operations (dry cleaning and solvent degreasing). The amount of solvent recovered from the waste varies from about 40 to 99 percent, depending on the extent and characterization of the contamination and on the recovery process employed.

Design parameters and economic factors determine whether solvent reclamation is accomplished as a main process by a private contractor, as an integral part of a main process (such as solvent refining), or as an added process (as in the surface coating and cleaning industries). Most contract solvent reprocessing operations recover halogenated hydrocarbons (e. g., methylene chloride, trichlorotrifluoroethane, and trichloroethylene) from degreasing, and/or aliphatic, aromatic, and naphthenic solvents such as those used in the paint and coatings industry. They may also reclaim small quantities of numerous specialty solvents such as phenols, nitriles, and oils.

The general reclamation scheme for solvent reuse is illustrated in Figure 4.7-1. Industrial operations may not incorporate all of these steps. For instance, initial treatment is necessary only when liquid waste solvents contain dissolved contaminants.

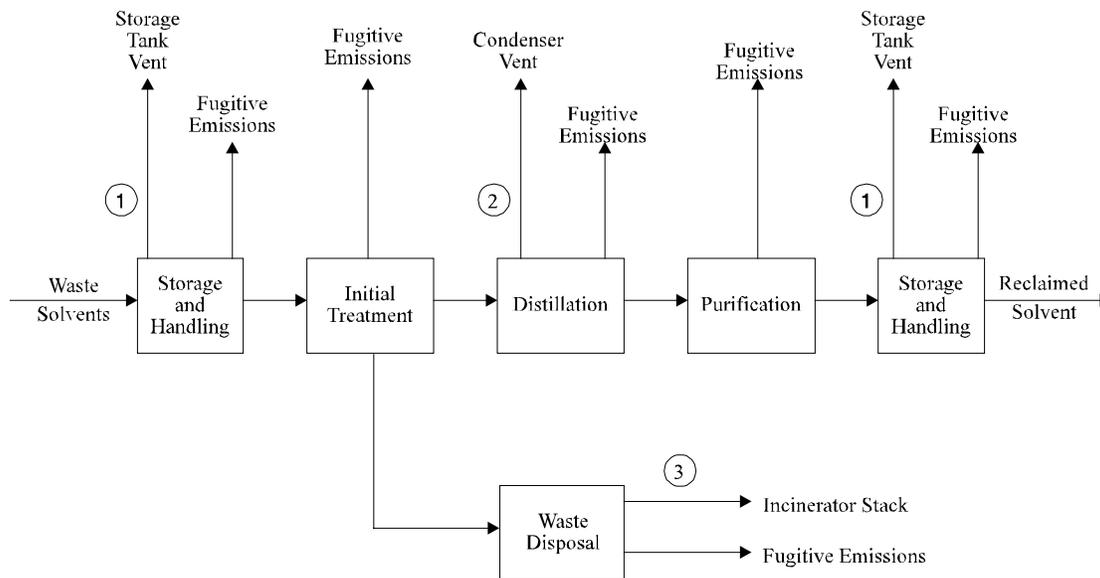


Figure 4.7-1. General waste solvent reclamation scheme and emission points.<sup>1</sup>

#### 4.7.1.1 Solvent Storage And Handling -

Solvents are stored before and after reclamation in containers ranging in size from 0.2-m<sup>3</sup> (55-gallon) drums to tanks with capacities of 75 m<sup>3</sup> (20,000 gallons) or more. Storage tanks are of fixed or floating roof design. Venting systems prevent solvent vapors from creating excessive pressure or vacuum inside fixed roof tanks.

Handling includes loading waste solvent into process equipment and filling drums and tanks prior to transport and storage. The filling is most often done through submerged or bottom loading.

#### 4.7.1.2 Initial Treatment -

Waste solvents are initially treated by vapor recovery or mechanical separation. Vapor recovery entails removal of solvent vapors from a gas stream in preparation for further reclaiming operations. In mechanical separation, undissolved solid contaminants are removed from liquid solvents.

Vapor recovery or collection methods employed include condensation, adsorption, and absorption. Technical feasibility of the method chosen depends on the solvent's miscibility, vapor composition and concentration, boiling point, reactivity, and solubility, as well as several other factors.

Condensation of solvent vapors is accomplished by water-cooled condensers and refrigeration units. For adequate recovery, a solvent vapor concentration well above 20 milligrams per cubic meter (mg/m<sup>3</sup>) (0.009 grains per cubic foot [gr/ft<sup>3</sup>]) is required. To avoid explosive mixtures of a flammable solvent and air in the process gas stream, air is replaced with an inert gas, such as nitrogen. Solvent vapors that escape condensation are recycled through the main process stream or recovered by adsorption or absorption.

Activated carbon adsorption is the most common method of capturing solvent emissions. Adsorption systems are capable of recovering solvent vapors in concentrations below 4 mg/m<sup>3</sup> (0.002 gr/ft<sup>3</sup>) of air. Solvents with boiling points of 200°C (290°F) or more do not desorb effectively with the low-pressure steam commonly used to regenerate the carbon beds. Figure 4.7-2 shows a flow diagram of a typical fixed-bed activated carbon solvent recovery system. The mixture of steam and solvent vapor passes to a water-cooled condenser. Water-immiscible solvents are simply decanted to separate the solvent, but water-miscible solvents must be distilled, and solvent mixtures must be both decanted and distilled. Fluidized bed operations are also in use.

Absorption of solvent vapors is accomplished by passing the waste gas stream through a liquid in scrubbing towers or spray chambers. Recovery by condensation and adsorption results in a mixture of water and liquid solvent, while absorption recovery results in an oil and solvent mixture. Further reclaiming procedures are required if solvent vapors are collected by any of these 3 methods.

Initial treatment of liquid waste solvents is accomplished by mechanical separation methods. This includes both removing water by decanting and removing undissolved solids by filtering, draining, settling, and/or centrifuging. A combination of initial treatment methods may be necessary to prepare waste solvents for further processing.

#### 4.7.1.3 Distillation -

After initial treatment, waste solvents are distilled to remove dissolved impurities and to separate solvent mixtures. Separation of dissolved impurities is accomplished by simple batch, simple continuous, or steam distillation. Mixed solvents are separated by multiple simple distillation methods, such as batch or continuous rectification. These processes are shown in Figure 4.7-3.

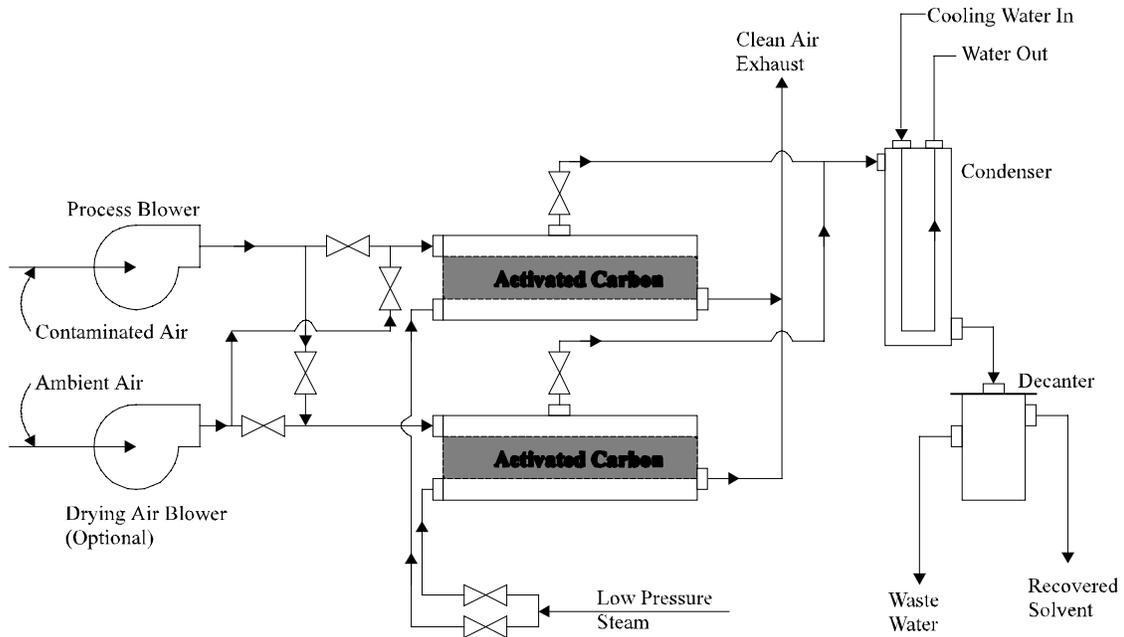


Figure 4.7-2. Typical fixed-bed activated carbon solvent recovery system.<sup>6</sup>

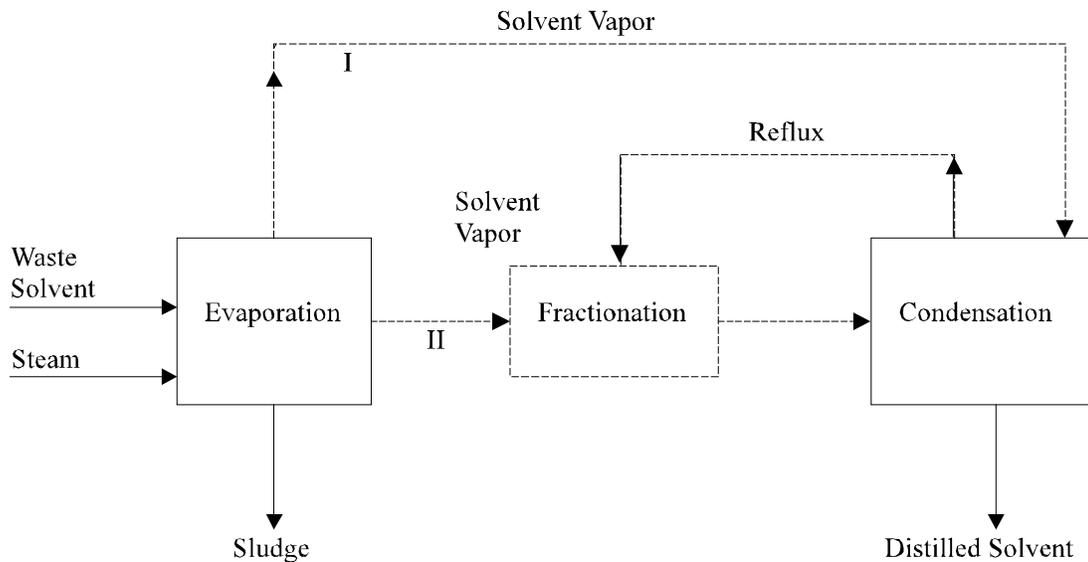


Figure 4.7-3. Distillation process for solvent reclaiming.<sup>1</sup>

In simple distillation, waste solvent is charged to an evaporator. Vapors are then continuously removed and condensed, and the resulting sludge or still bottoms are drawn off. In steam distillation, solvents are vaporized by direct contact with steam which is injected into the evaporator. Simple batch, continuous, and steam distillations follow Path I in Figure 4.7-3.

The separation of mixed solvents requires multiple simple distillation or rectification. Batch and continuous rectification are represented by Path II in Figure 4.7-3. In batch rectification, solvent vapors pass through a fractionating column, where they contact condensed solvent (reflux) entering at the top of the column. Solvent not returned as reflux is drawn off as overhead product. In continuous rectification, the waste solvent feed enters continuously at an intermediate point in the column. The more volatile solvents are drawn off at the top, while those with higher boiling points collect at the bottom.

Design criteria for evaporating vessels depend on waste solvent composition. Scraped surface stills or agitated thin film evaporators are the most suitable for heat sensitive or viscous materials. Condensation is accomplished by barometric or shell and tube condensers. Azeotropic solvent mixtures are separated by the addition of a third solvent component, while solvents with higher boiling points, e. g., in the range of high-flash naphthas (155°C, 310°F), are most effectively distilled under vacuum. Purity requirements for the reclaimed solvent determine the number of distillations, reflux ratios, and processing time needed.

#### 4.7.1.4 Purification -

After distillation, water is removed from solvent by decanting or salting. Decanting is accomplished with immiscible solvent and water which, when condensed, form separate liquid layers, 1 or the other of which can be drawn off mechanically. Additional cooling of the solvent/water mix before decanting increases the separation of the 2 components by reducing their solubility. In salting, solvent is passed through a calcium chloride bed, and water is removed by absorption.

During purification, reclaimed solvents are stabilized, if necessary. Buffers are added to virgin solvents to ensure that pH level is kept constant during use. To renew it, special additives are used during purification. The composition of these additives is considered proprietary.

#### 4.7.1.5 Waste Disposal -

Waste materials separated from solvents during initial treatment and distillation are disposed of by incineration, landfilling, or deep well injection. The composition of such waste varies, depending on the original use of the solvent. But up to 50 percent is unreclaimed solvent, which keeps the waste product viscous yet liquid, thus facilitating pumping and handling procedures. The remainder consists of components such as oils, greases, waxes, detergents, pigments, metal fines, dissolved metals, organics, vegetable fibers, and resins.

About 80 percent of the waste from solvent reclaiming by private contractors is disposed of in liquid waste incinerators. About 14 percent is deposited in sanitary landfills, usually in 55-gallon drums. Deep well injection is the pumping of wastes between impermeable geologic strata. Viscous wastes may have to be diluted for pumping into the desired stratum level.

### 4.7.2 Emissions And Controls<sup>1,3-5</sup>

Volatile organic and particulate emissions result from waste solvent reclamation. Emission points include storage tank vents [1], condenser vents [2], incinerator stacks [3], and fugitive losses (numbers refer to Figure 4.7-1 and Figure 4.7-3). Emission factors for these sources are given in Table 4.7-1.

Solvent storage results in volatile organic compound (VOC) emissions from solvent evaporation (Figure 4.7-1, emission point 1). The condensation of solvent vapors during distillation (Figure 4.7-3) also involves VOC emissions, and if steam ejectors are used, emission of steam and noncondensables as well (Figure 4.7-1 and Figure 4.7-3, point 2). Incinerator stack emissions consist

Table 4.7-1 (Metric And English Units). EMISSION FACTORS FOR SOLVENT RECLAIMING<sup>a</sup>

EMISSION FACTOR RATING: D

Source	Criteria Pollutant	Emission Factor Average	
		kg/Mg	lb/ton
Storage tank vent <sup>b</sup>	Volatile organics	0.01 (0.002 - 0.04)	0.02 (0.004 - 0.09)
Condenser vent	Volatile organics	1.65 (0.26 - 4.17)	3.30 (0.52 - 8.34)
Incinerator stack <sup>c</sup>	Volatile organics	0.01	0.02
Incinerator stack	Particulates	0.72 (0.55 - 1.0)	1.44 (1.1 - 2.0)
Fugitive emissions			
Spillage <sup>c</sup>	Volatile organics	0.10	0.20
Loading	Volatile organics	0.36 (0.00012 - 0.71)	0.72 (0.00024 - 1.42)
Leaks	Volatile organics	ND	ND
Open sources	Volatile organics	ND	ND

<sup>a</sup> Reference 1. Data obtained from state air pollution control agencies and presurvey sampling. All emission factors are for uncontrolled process equipment, except those for the incinerator stack. (Reference 1 does not, however, specify what the control is on this stack.) Average factors are derived from the range of data points available. Factors for these sources are given in terms of kilograms per megagram and pounds per ton of reclaimed solvent. Ranges in parentheses. ND = no data.

<sup>b</sup> Storage tank is of fixed roof design.

<sup>c</sup> Only 1 value available.

of solid contaminants that are oxidized and released as particulates, unburned organics, and combustion stack gases (Figure 4.7-1, point 3).

VOC emissions from equipment leaks, open solvent sources (sludge drawoff and storage from distillation and initial treatment operations), solvent loading, and solvent spills are classified as fugitive. The former 2 sources are continuously released, and the latter 2, intermittently.

Solvent reclamation is viewed by industry as a form of control in itself. Carbon adsorption systems can remove up to 95 percent of the solvent vapors from an air stream. It is estimated that less than 50 percent of reclamation plants run by private contractors use any control technology.

Volatile organic emissions from the storage of solvents can be reduced by as much as 98 percent by converting from fixed to floating roof tanks, although the exact percent reduction also

depends on solvent evaporation rate, ambient temperature, loading rate, and tank capacity. Tanks may also be refrigerated or equipped with conservation vents which prevent air inflow and vapor escape until some preset vacuum or pressure develops.

Solvent vapors vented during distillation are controlled by scrubbers and condensers. Direct flame and catalytic afterburners can also be used to control noncondensables and solvent vapors not condensed during distillation. The time required for complete combustion depends on the flammability of the solvent. Carbon or oil adsorption may be employed also, as in the case of vent gases from the manufacture of vegetable oils.

Wet scrubbers are used to remove particulates from sludge incinerator exhaust gases, although they do not effectively control submicron particles.

Submerged rather than splash filling of storage tanks and tank cars can reduce solvent emissions from this source by more than 50 percent. Proper plant maintenance and loading procedures reduce emissions from leaks and spills. Open solvent sources can be covered to reduce these fugitive emissions.

#### References For Section 4.7

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